corresponding bond angles in **1a–c**.

Conclusion

All three possible structural isomers of 1,5-diphosphadithiatetrazocines are formed in the reaction of reagents of the type $RR'PN_2(SiMe_3)_3$ with $SOCl_2$ or SCl_2. The major product is the unsymmetrical isomer in which one R group and one R′ group occupy *endo* positions. The predominant symmetrical isomer has the least sterically demanding groups in the *endo* positions. The 1,5-diphosphadithiatetrazocines **2b**, **3b**, and **4b** represent the first examples of this ring system with exocyclic P–Cl linkages. As such they provide a unique opportunity to investigate reactions at phosphorus rather than at the sulfur or nitrogen centers of these hybrid ring systems.

Acknowledgment. We thank the NSERC (Canada) for financial support.

Registry No. **1b**, 80106-10-1; **1c**, 140360-67-4; **2a**, 140360-65-2; **2b**, 140360-66-3; **2c**, 140360-68-5; **3a**, 140461-02-5; **3b**, 140460-06-6; **3c**, 140460-08-8; **4a**, 140460-05-5; **4b**, 140460-07-7; **4c**, 140460-09-9; $Me(Ph)PN_2(SiMe_3)_3$, 69687-06-5; $Cl_3C(Cl)PN_2(SiMe_3)_3$, 50732-23-5; $Et(I)PN_2(SiMe_3)_3$, 58971-96-3; $Ph_2PN_2(SiMe_3)_3$, 61500-31-0; $Et_2PN_2(SiMe_3)_3$, 140360-69-6.

Supplementary Material Available: Tables listing thermal parameters and dihedral angles for **1c** and **2b** and hydrogen coordinates and isotropic thermal parameters for **1c** (6 pages); tables of calculated and observed structure factors for **1c** and **2b** (35 pages). Ordering information is given on any current masthead page.

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Structure and Bonding, Texas A&M University, College Station, Texas 77843

Comparison of the Crystalline Adducts of Tetrakis(triphenylacetato)dichromium(II) with Benzene, *p*-Difluorobenzene, and *p*-Xylene

F. Albert Cotton,* Lee M. Daniels, and Piotr A. Kibala

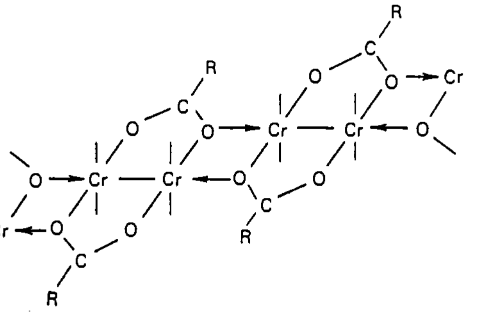
Received November 14, 1991

For comparison with the previously described $Cr_2(O_2CCPh_3)_4{\cdot}C_6H_6$ ($1{\cdot}C_6H_6$), we have prepared and structurally characterized analogues with p-$C_6H_4F_2$ and p-$C_6H_4(CH_3)_2$ in place of benzene. These new compounds are essentially isostructural with $1{\cdot}C_6H_6$ and have the following crystallographic characteristics. $1{\cdot}{}^3/_2C_6H_4F_2$: space group, $P4_2/nnc$, $a = 20.698$ (6) Å, $c = 17.903$ (8) Å, $V = 7670$ (8) Å^3, $Z = 4$. In addition to the $C_6H_4F_2$ molecules perpendicular to the c axis and stacked alternately with the molecules of **1**, there are two additional and highly disordered $C_6H_4F_2$ molecules in each unit cell. The Cr–Cr and Cr–ring center distances for $1{\cdot}{}^3/_2C_6H_4F_2$ are 2.176 (3) and 3.39 (1) Å, respectively. $1{\cdot}C_6H_4Me_2{\cdot}C_6H_{14}$: space group, $P4_2/ncc$, $a = 20.695$ (6) Å, $b = 17.820$ (6) Å, $V = 7632$ (7) Å^3, $Z = 4$. In addition to the alternating parallel chains of **1** and $C_6H_4Me_2$ molecules, there are disordered hexane molecules present. The Cr–Cr and Cr–ring center distances are 2.291 (3) and 3.31 (1) Å, respectively. These results, which bracket those (2.256 (4) and 3.30 (1) Å) for $1{\cdot}C_6H_6$, are discussed in terms of the interactions between the molecules of **1** and the π orbitals of the C_6H_6, $C_6H_4F_2$, and $C_6H_4Me_2$ molecules. Attempts to structurally characterize analogous compounds with durenes C_6Me_6, $C_6H_2F_4$, and C_6F_6 were unsuccessful. The short Cr–Cr distance in $1{\cdot}{}^3/_2C_6H_4F_2$ provides indirect support for the correctness of the very short distances in gaseous $Cr_2(O_2CCH_3)_4$. Several factors responsible for the variation in Cr–Cr distances will be discussed.

Introduction

The multiple bonds between chromium atoms[1] are among the more interesting curiosities of contemporary chemistry, but they are common enough and important enough that they are not *mere* curiosities. One of their greatest peculiarities is that in spite of being highly multiple (at least formally), namely, of order six in Cr_2, four in numerous Cr_2^{4+} complexes, or three in $Cr_2(tmtaa)_2$,[2] and among the shortest bonds (relative to the intrinsic size of the atoms) known, they are not very strong. They have also proven extremely troublesome from a theoretical point of view because there is so much electron correlation that extraordinary (and new) approaches have been necessary to obtain reasonable descriptions of them.[3,4]

One particular problem in this area has to do with the influence of axial ligands on the Cr–Cr bond in $Cr_2(LL)_4X_2$ compounds, where LL represents a bridging bidentate ligand (e.g., RCO_2^-) and X is an axially coordinated ligand. Several years ago in an effort to obtain in crystalline form a $Cr_2(O_2CR)_4$-type molecule without axial ligation, we prepared $Cr_2(O_2CCPh_3)_4$ and crystallized it from benzene.[5] The idea here was that the bulky CPh_3 groups would prevent the type of intermolecular association which normally occurs (see I) in $Cr_2(O_2CR)_4$ compounds with R = CH_3,[6] CMe_3,[7] and o-PhC_6H_4[8] and no exogenous ligand would be available either. This strategy proved to be only partially effective. The bulk of the CPh_3 groups did lead to a packing arrangement in the crystal such that no intermolecular contacts between an oxygen atom of one molecule and the axial position of a neighbor occurred. However, benzene molecules were incorporated into the crystal in such a way that they served as a very unusual type of axial ligand, as shown schematically in II.



(I)

A theoretical analysis[5] of the nature of the axial interaction of the benzene molecules with the $Cr_2(O_2CCPh_3)_4$ molecules showed that while there are several components, the one that has the greatest effect on the Cr–Cr distance is donation from the

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(1) Cotton, F. A.; Walton, R. A. *Multiple Bonds Between Metal Atoms*; John Wiley & Sons: New York, 1982; Chapter 4.

(2) Cotton, F. A.; Czuchajowska, J.; Feng, X. *Inorg. Chem.* **1990**, *29*, 4329.

(3) Salahub, D. R. *Adv. Chem. Phys.* **1987**, *69*, 447 (where, from a theoretical point of view, Cr_2 is described as both a cause célèbre and a bête noire).

(4) Hall, M. B. *Polyhedron* **1987**, *6*, 697.

(5) Cotton, F. A.; Feng, X.; Kibala, P. A.; Matusz, M. *J. Am. Chem. Soc.* **1988**, *110*, 2807.

(6) Cotton, F. A.; Rice, C. E.; Rice, G. W. *J. Am. Chem. Soc.* **1977**, *99*, 4704.

(7) Cotton, F. A.; Extine, M. W.; Rice, G. W. *Inorg. Chem.* **1978**, *17*, 176.

(8) Cotton, F. A.; Thompson, J. L. *Inorg. Chem.* **1981**, *20*, 1292.

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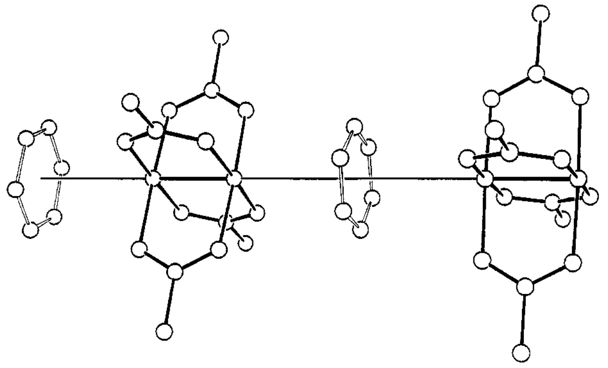

(II)

filled degenerate ring π orbital (e_{1g}) to the π^*(Cr–Cr) orbital. From this analysis, it was logical to suppose that upon replacing the benzene molecules by substituted benzene molecules, the Cr–Cr and Cr–ring center distances could be altered according to the inductive effect of the substituents. Specifically, it would be expected that, compared to C_6H_6, a $C_6H_{6-n}Me_n$ molecule would give a longer Cr–Cr and a shorter Cr–ring center distance, while a $C_6H_{6-n}F_n$ molecule would give a shorter Cr–Cr and a longer Cr–ring center distance.

The results reported here were the only positive ones obtained by attempting to put these concepts into experimental form. Unfortunately, it appears that the constraints imposed by the crystal packing are fairly severe and other molecules (1,2,4,5-$C_6H_2Me_4$, C_6Me_6, $C_6H_2F_4$, C_6F_6) failed to give useful crystalline materials. The two compounds that have been obtained and studied give at least qualitative support to the general concepts that were derived from the study of the benzene compound, but it turns out that because of variations in the unit cell size, and perhaps other factors, a simple quantitative relationship between the Cr–Cr distances and the ionization potentials of arenes does not emerge.

Experimental Section

Preparation of Compounds. Bis(cyclopentadienyl)chromium, sublimed grade was purchased from Strem Chemical Co., triphenylacetic acid, xylene, durene, hexamethylbenzene, difluorobenzene, tetrafluorobenzene, and hexafluorobenzene were purchased from Aldrich Chemical Co., and all were used as received. All manipulations were done in Schlenkware with exclusion of air and water.

Both compounds, $Cr_2(O_2CCPh_3)_4{\cdot}C_6H_4F_2$ and $Cr_2(O_2CCPh_3)_4{\cdot}C_6H_4Me_2$, were prepared in the same way, on an approximately millimolar scale. Either pure arene or a mixture of arene and hexane was used to make a solution of $(C_5H_5)_2Cr$ and one of Ph_3CCO_2H. About 10 mL of the acid solution was placed in a Schlenk tube and a similar quantity of the bis(cyclopentadienyl) chromium solution was placed on top of it, keeping the two layers as unmixed as possible. Over a period of several weeks the products appeared in crystalline form. Yields were nearly quantitative.

The durene, tetrafluorobenzene, and hexafluorobenzene compounds were prepared similarly, while in the case of hexamethylbenzene, a large amount of hexane was used as a solvent. In these four cases, products formed in what appeared to be high yield, but only small, badly-formed crystals were ever found and no further work could be done with them.

X-ray Crystallography. The methods used were essentially the same as those previously described.[5] In the final stages of refinement, however, each of the present compounds presented certain problems because of disorder. These will be discussed in the Results section. The general information as to crystallographic characteristics, data collection, and refinement is given in Table I, and the positional parameters are listed in Tables II and III.

Results

For $Cr_2(O_2CCPh_3)_4{\cdot}C_6H_4F_2$ the space group was uniquely determined to be $P4_2/nnc$, and the two component molecules were found to form alternating chains along $^1/_4$, $^3/_4$, z and $^3/_4$, $^1/_4$, z. This portion of the structure was handled straightforwardly and displayed no disorder or other problematical characteristic. However, two more $C_6H_4F_2$ molecules were located between these stacks on and perpendicular to the crystallographic tetrad axis. The para F atoms in this molecule were disordered over all three possible positions, in addition to the disorder imposed by the 4-fold axis. The result is a *p*-difluorobenzene molecule evenly distributed over six distinct orientations. In order to refine this model successfully, the C–C and C–F distances were included as observations in the least squares calculations as 1.395 (2) and 1.363 (2) Å, respectively.[9]

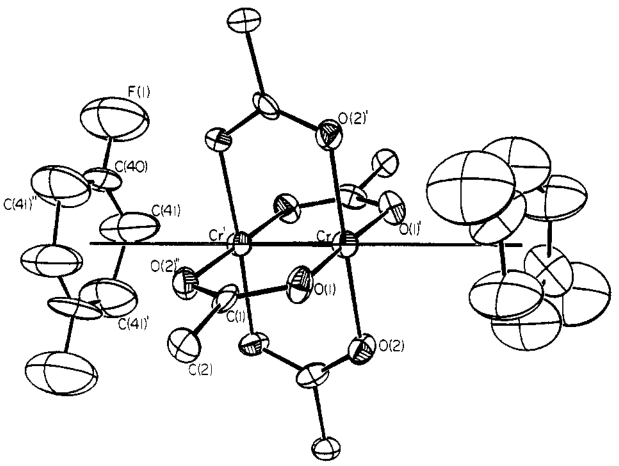

Figure 1. Segment of the chain made up of $Cr_2(O_2CCPh_3)_4{\cdot}C_6H_4F_2$ units. Phenyl groups on the β-carbon atoms have been omitted for clarity.

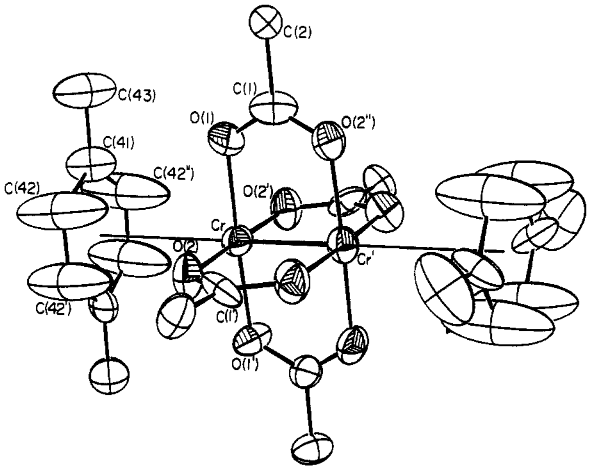

Figure 2. Segment of the chain made up of $Cr_2(O_2CCPh_3)_4{\cdot}C_6H_4Me_2$ units. Phenyl groups on the β-carbon atoms have been omitted for clarity.

The phenyl rings of the triphenylacetate group were refined as rigid groups having bond lengths of 1.395 Å and bond angles of 120°. In the final stages of refinement, all of the atoms in the ordered stacks were given anisotropic temperature factors, while the other solvent molecule was left isotropic. Hydrogen atoms, which were added in idealized positions for the phenyl rings of the triphenylacetate group, were included in the calculation of structure factors, but not refined.

Figure 1 shows a segment of the ordered chain, but excluding for clarity the phenyl groups on the β-carbon atoms. It should be noted that the stacking axes are 4_2 symmetry axes, and thus the ring orientations alternate. Moreover, the fluorine atoms are placed so as to be staggered with respect to the adjacent CrO_4 moieties. Selected distances and angles are given in Table IV.

For $Cr_2(O_2CCPh_3)_4{\cdot}C_6H_4Me_2$ the space group was again uniquely determined, but this time it is $P4_2/ncc$. The $C_6H_4Me_2$ groups are again alternately rotated by 90°, one to the next, but this time they have the substituents (the CCH_3 units) aligned with the adjacent CrO_4 moieties (that is, eclipsed rather than staggered relative to the Cr–O bonds). This is shown in Figure 2, and the principal distances and angles are listed in Table V.

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[9] Orpen, A. G.; Brammer, L.; Allen, F. H.; Kennard, O.; Watson, D. G.; Taylor, R. *J. Chem. Soc., Dalton Trans.* **1989**, S1.

Table I. Crystal Data for $Cr_2(O_2CCPh_3)_4{\cdot}C_6H_4F_2$ and $Cr_2(O_2CCPh_3)_4{\cdot}C_6H_4Me_2$

	$\mathbf{1}{\cdot}{}^3/_2C_6H_4F_2$	$\mathbf{1}{\cdot}C_6H_4Me_2{\cdot}C_6H_{14}$
formula	$Cr_2F_2O_8C_{86}H_{64}{\cdot}{}^1/_2C_6F_2H_4$	$Cr_2O_8C_{88}H_{70}{\cdot}C_6H_{14}$
fw	1424.50	1445.70
space group	$P4_2/nnc$	$P4_2/ncc$
a, Å	20.698 (6)	20.695 (6)
c, Å	17.903 (8)	17.820 (6)
V, Å^3	7670 (8)	7632 (7)
Z	4	4
d_{calcd}, g/cm^3	1.234	1.258
crystal size, mm	0.4 × 0.3 × 0.2	0.25 × 0.35 × 0.20
μ(Mo Kα), cm^{-1}	3.357	3.329
data collctn instrument	P3/F equiv	Rigaku AFC5R
radiatn (monochromated in incident beam)	Mo Kα (λ_α = 0.710 73 Å)	
orientation reflns: no., range (2θ)	19, 15.0–24.9	25, 20.0–28.2
temp, °C	22 (1)	22 (2)
scan method	ω–2θ	ω–2θ
data collectn range (2θ), deg	4.0–45.0	4.0–45.0
total no. of unique data	2507	2511
with $F_o^2 > 3\sigma(F_o^2)$	867	926
N (parameters)	199	205
transm factors: max, min	0.9977, 0.9601	1.000, 0.986
R^a	0.062	0.069
$R_w{}^b$	0.080	0.091
quality of fit indicator^c	1.94	1.85
largest shift/esd, final cycle	0.11	0.02
largest peak, e/Å^3	0.49 (4)	0.54 (7)

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$. [c] Quality of fit, $[\sum w(|F_o| - |F_c|)^2/(N_{obs} - N_{parameters})]^{1/2}$.

Table II. Positional Parameters and Their Estimated Standard Deviations for $Cr_2(O_2CCPh_3)_4{\cdot}{}^3/_2C_6H_4F_2{}^a$

atom	x	y	z	B, Å^2
Cr	0.250	0.750	0.0608 (1)	4.08 (7)
O(1)	0.3233 (3)	0.6890 (4)	0.0638 (5)	4.9 (3)
O(2)	0.3243 (4)	0.6885 (4)	−0.0606 (5)	5.1 (2)
C(1)	0.3442 (5)	0.6697 (5)	0.001 (1)	4.6 (3)
C(2)	0.3983 (5)	0.6148 (5)	0.0042 (7)	4.7 (3)
C(10)	0.4483 (4)	0.6302 (5)	0.0646 (4)	5.0 (3)
C(11)	0.4795 (4)	0.5800 (5)	0.1021 (4)	5.9 (4)
C(12)	0.5277 (4)	0.5938 (5)	0.1541 (4)	6.8 (4)
C(13)	0.5447 (4)	0.6577 (5)	0.1688 (4)	8.9 (5)
C(14)	0.5135 (4)	0.7079 (5)	0.1312 (4)	8.0 (5)
C(15)	0.4654 (4)	0.6941 (5)	0.0792 (4)	6.8 (4)
C(20)	0.3623 (5)	0.5511 (4)	0.0267 (7)	6.3 (4)
C(21)	0.3747 (5)	0.4943 (4)	−0.0127 (7)	8.2 (4)
C(22)	0.3443 (5)	0.4369 (4)	0.0081 (7)	10.4 (6)
C(23)	0.3015 (5)	0.4363 (4)	0.0683 (7)	11.4 (7)
C(24)	0.2891 (5)	0.4932 (4)	0.1076 (7)	9.8 (5)
C(25)	0.3195 (5)	0.5505 (4)	0.0868 (7)	7.3 (4)
C(30)	0.4288 (5)	0.6078 (4)	−0.0733 (4)	5.4 (3)
C(31)	0.3916 (5)	0.5945 (4)	−0.1364 (4)	7.1 (4)
C(32)	0.4209 (5)	0.5909 (4)	−0.2065 (4)	9.4 (5)
C(33)	0.4873 (5)	0.6005 (4)	−0.2134 (4)	9.1 (5)
C(34)	0.5245 (5)	0.6138 (4)	−0.1503 (4)	8.3 (5)
C(35)	0.4953 (5)	0.6174 (4)	−0.0802 (4)	6.3 (4)
F(1)	0.376 (1)	0.750	0.250	22.9 (8)
C(40)	0.312 (1)	0.750	0.250	20 (1)
C(41)	0.282 (1)	0.688 (2)	0.257 (2)	22 (1)
F(2)	0.393 (3)	0.250	0.250	16 (3)*
F(2′)	0.315 (4)	0.140 (3)	0.250	5 (2)*
C(50)	0.327 (3)	0.250	0.250	11 (1)*
C(51)	0.284 (2)	0.198 (2)	0.250	10 (1)*

[a] Anisotropically refined atoms are given in the form of the equivalent isotropic displacement parameter defined as $^1/_3[a^2a^{*2}B_{11} + b^2b^{*2}B_{22} + c^2c^{*2}B_{33} + 2ab(\cos\gamma)a^*b^*B_{12} + 2ac(\cos\beta)a^*c^*B_{13} + 2bc(\cos\alpha)b^*c^*B_{23}]$. Starred atoms were refined isotropically.

Table III. Positional Parameters and Their Estimated Standard Deviations for $Cr_2(O_2CCPh_3)_4{\cdot}C_6H_4Me_2{\cdot}C_6H_{14}{}^a$

atom	x	y	z	B, Å^2
Cr	0.250	0.750	0.0643 (1)	3.08 (6)
O(1)	0.3098 (4)	0.6737 (4)	0.0618 (6)	4.0 (3)
O(2)	0.1740 (4)	0.6914 (4)	0.0618 (6)	4.0 (3)
C(1)	0.3277 (5)	0.6513 (5)	−0.001 (1)	3.7 (3)
C(2)	0.3783 (5)	0.5946 (5)	−0.001 (1)	3.9 (3)
C(10)	0.3693 (5)	0.5540 (4)	0.0724 (4)	4.1 (4)
C(11)	0.4227 (5)	0.5342 (4)	0.1142 (4)	4.6 (4)
C(12)	0.4143 (5)	0.4945 (4)	0.1767 (4)	5.7 (4)
C(13)	0.3525 (5)	0.4746 (4)	0.1974 (4)	6.6 (5)
C(14)	0.2990 (5)	0.4944 (4)	0.1557 (4)	5.8 (4)
C(15)	0.3074 (5)	0.5341 (4)	0.0932 (4)	4.5 (4)
C(20)	0.3727 (5)	0.5500 (4)	−0.0704 (5)	4.3 (4)
C(21)	0.3608 (5)	0.5739 (4)	−0.1422 (5)	8.5 (6)
C(22)	0.3565 (5)	0.5316 (4)	−0.2029 (5)	8.7 (6)
C(23)	0.3641 (5)	0.4653 (4)	−0.1918 (5)	5.9 (5)
C(24)	0.3760 (5)	0.4414 (4)	−0.1199 (5)	6.1 (4)
C(25)	0.3803 (5)	0.4837 (4)	−0.0592 (5)	5.3 (4)
C(30)	0.4446 (3)	0.6310 (4)	0.0019 (6)	4.7 (3)
C(31)	0.4913 (3)	0.6185 (4)	−0.0527 (6)	5.8 (4)
C(32)	0.5509 (3)	0.6498 (4)	−0.0496 (6)	7.2 (5)
C(33)	0.5639 (3)	0.6936 (4)	0.0079 (6)	7.3 (5)
C(34)	0.5172 (3)	0.7061 (4)	0.0625 (6)	6.6 (5)
C(35)	0.4575 (3)	0.6748 (4)	0.0594 (6)	4.8 (4)
C(41)	0.2993 (6)	0.701	0.254	4.6 (4)
C(42)	0.2367 (7)	0.6886 (8)	0.251 (2)	15 (1)
C(43)	0.3495 (7)	0.651	0.250	7.5 (5)
C(101)	0.250	0.250	0.110 (5)	6.2 (6)*
C(102)	0.298 (3)	0.230 (3)	0.154 (3)	6.2 (6)*
C(103)	0.250	0.250	0.234 (1)	6.2 (6)*
C(104)	0.266 (3)	0.305 (2)	0.318 (3)	6.2 (6)*
C(105)	0.250	0.250	0.339 (3)	6.2 (6)*
C(106)	0.250	0.250	0.418 (5)	6.2 (6)*

[a] Anisotropically refined atoms are given in the form of the equivalent isotropic displacement parameter defined as $^1/_3[a^2a^{*2}B_{11} + b^2b^{*2}B_{22} + c^2c^{*2}B_{33} + 2ab(\cos\gamma)a^*b^*B_{12} + 2ac(\cos\beta)a^*c^*B_{13} + 2bc(\cos\alpha)b^*c^*B_{23}]$. Starred atoms were refined isotropically.

In $Cr_2(O_2CCPh_3)_4{\cdot}C_6H_4Me_2$ there were also highly disordered molecules between the ordered stacks. These were modeled as hexane molecules although it cannot be said definitively that that is what they were. No arrangement of xylene molecules was found that behaved as well.

Because of the limited number of observed data, all of the phenyl rings of the Ph_3CCO_2 entity were refined as rigid groups having C–C bond lengths of 1.395 Å and bond angles of 120°. In the final stages of refinement, all of the atoms of the metal complex were given anisotropic temperature factors. A common temperature factor was refined for all six of the carbon atoms of the disordered lattice solvent molecule. Hydrogen atoms were added in idealized positions (1.08 Å from the respective carbon atoms) for the phenyl rings. Hydrogen atom positions were used only for the calculation of structure factors, while a single common temperature factor was refined.

Table IV. Bond Distances (Å) and Angles (deg) for $Cr_2(O_2CCPh_3)_4 \cdot {}^3/_2C_6H_4F_2$[a]

Cr–Cr′	2.176 (3)	C(2)–C(30)	1.53 (1)
Cr–O(1)	1.975 (7)	F(1)–C(40)	1.32 (4)
Cr–O(2)	1.995 (8)	C(40)–C(41)	1.43 (3)
O(1)–C(1)	1.27 (2)	C(41)–C(41′)	1.35 (3)
O(2)–C(1)	1.24 (2)	C(50)–C(51)	1.40 (5)
C(1)–C(2)	1.60 (1)	C(51)–F(2′)	1.36 (9)
C(2)–C(10)	1.53 (1)	C(50)–F(2)	1.36 (8)
C(2)–C(20)	1.57 (1)	Cr–BzF2[b]	3.388 (2)
Cr′–Cr–O(1)	91.6 (3)	C(1)–C(2)–C(20)	106.0 (8)
Cr′–Cr–O(2)	90.0 (3)	C(1)–C(2)–C(30)	109 (1)
O(1)–Cr–O(1′)	176.8 (4)	C(10)–C(2)–C(20)	108.3 (9)
O(1)–Cr–O(2)	90.1 (3)	C(10)–C(2)–C(30)	112.3 (8)
O(1)–Cr–O(2′)	89.9 (3)	C(20)–C(2)–C(30)	110.6 (9)
O(2)–Cr–O(2′)	180 (0)	F(1)–C(40)–C(41)	116 (1)
Cr–O(1)–C(1)	116.0 (8)	C(41)–C(40)–C(41″)	128 (3)
Cr–O(2)–C(1′)	117.1 (8)	C(40)–C(41)–C(41′)	115 (3)
O(1)–C(1)–O(2″)	125 (1)	C(51)–C(50)–C(51′)	100 (4)
O(1)–C(1)–C(2)	116 (1)	C(51)–C(50)–F(2)	130 (2)
O(2)–C(1′)–C(2′)	119 (1)	C(50)–C(51)–F(2′)	112 (5)
C(1)–C(2)–C(10)	111 (1)		

[a] Numbers in parentheses are estimated standard deviations in the least significant digits. [b] BzF2 represents the centroid of the axially-coordinated *p*-difluorobenzene entity.

Table V. Bond Distances (Å) and Angles (deg) for $Cr_2(O_2CCPh_3)_4 \cdot C_6H_4Me_2 \cdot C_6H_{14}$[a]

Cr–Cr′	2.291 (3)	C(2)–C(20)	1.55 (2)
Cr–O(1)	2.008 (8)	C(2)–C(30)	1.56 (1)
Cr–O(2)	1.987 (9)	C(41)–C(42)	1.32 (2)
O(1)–C(1)	1.26 (2)	C(41)–C(43)	1.47 (2)
O(2)–C(1)	1.25 (2)	C(42)–C(42′)	1.41 (2)
C(1)–C(2)	1.57 (1)	Cr–Xy(c)[b]	3.310 (2)
C(2)–C(10)	1.56 (2)		
Cr′–Cr–O(1)	88.7 (3)	C(1)–C(2)–C(30)	103.0 (7)
Cr′–Cr–O(2)	88.7 (3)	C(10)–C(2)–C(20)	109.8 (8)
O(1)–Cr–O(1′)	177.4 (4)	C(10)–C(2)–C(30)	110 (1)
O(1)–Cr–O(2)	90.4 (4)	C(20)–C(2)–C(30)	112 (1)
O(1)–Cr–O(2′)	89.5 (4)	C(2)–C(10)–C(11)	120.5 (9)
O(2)–Cr–O(2′)	177.5 (4)	C(2)–C(10)–C(15)	119.4 (8)
Cr–O(1)–C(1)	119.2 (9)	C(2)–C(20)–C(21)	122.5 (9)
Cr–O(2)–C(1′)	120.7 (9)	C(2)–C(20)–C(25)	117.5 (9)
O(1)–C(1)–O(2″)	123 (1)	C(2)–C(30)–C(31)	119.9 (9)
O(1)–C(1)–C(2)	118 (2)	C(2)–C(30)–C(35)	120.1 (9)
O(2″)–C(1)–C(2)	120 (2)	C(42)–C(41)–C(42′)	112 (1)
C(1)–C(2)–C(10)	109 (1)	C(42)–C(41)–C(43)	124 (1)
C(1)–C(2)–C(20)	113 (1)	C(41)–C(42)–C(42′)	124 (1)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits. [b] Xy(c) represents the centroid of the axially-coordinated *p*-xylene entity.

Discussion

This work was carried out in the hope that by employing arenes with donor substituents (CH_3) and electronegative substituents (F) we could cause corresponding increases and decreases respectively, in the Cr–Cr distance. We have, in fact, observed such changes. We had also hoped that a quantitative correlation between the Cr–Cr bond lengths and the ionization potentials of the axial arenes would be observed. This quantitative goal has not been achieved, as the data in Table VI show.

Turning first to qualitative matters, as the ionization potentials of the arenes decrease, indicating greater availability of the electrons in the e_{1g} ring π orbital, the Cr–Cr bond becomes longer. This is qualitatively consistent with increased introduction of electron density into the π^* orbitals of the $Cr_2(O_2CCPh_3)_4$ molecule and is thus the expected qualitative effect. It is particularly interesting to note that the compound with p-$C_6H_4F_2$ now replaces the previously reported compound with benzene[5] as the one having the shortest Cr–Cr bond in an axially ligated $Cr_2(O_2CR)_4$ unit. The distance here is only 2.176 (3) Å, and this is of some importance in itself.

There is a long and unsatisfying history of attempts to account theoretically for the bonding in $Cr_2{}^{4+}$-containing molecules.[4] The greatest difficulty has been encountered for $Cr_2(O_2CR)_4L_n$ species, where most calculations[10] get Cr–Cr distances that are *far* too long (compared to the experimental value of 1.97 (1) Å for $Cr_2(O_2CCH_3)_4$[11]), although in one case,[12] a value even shorter than this was obtained, 1.87 Å. As a result of the large differences between the theoretical results and the experimental value obtained by gas-phase electron diffraction, skepticism as to the reliability of the latter has not been entirely absent. The present result shows that the value for a free $Cr_2(O_2CR)_4$ molecule must be below (and probably substantially below) 2.17 Å, thus supporting the experimental result for $Cr_2(O_2CCH_3)_4$ and indicating that the theoretical work is still seriously wanting, at least with respect to predicting Cr–Cr bond lengths.

Table VI. Arene Ionization Potentials and Structure Parameters

				dist in $Cr_2(O_2CCPh_3)_4$ arene, Å	
arene	first IP,[a] eV	unit cell *c* axis, Å	ctr to ctr dist,[b]	Cr–Cr	Cr–ring ctr
p-$C_6H_4F_2$	9.33	17.903 (8)	4.476 (2)	2.176 (3)	3.388 (2)
C_6H_6	9.25	17.710 (3)	4.428 (1)	2.256 (4)	3.299 (2)
p-$C_2H_4Me_2$	8.73	17.820 (6)	4.455 (2)	2.291 (3)	3.310 (2)

[a] Turner, D. W. *Molecular Photoelectron Spectroscopy*; Wiley-Interscience, New York, 1970. [b] Distance from the midpoint of the Cr–Cr bond to the midpoint of the arene ring.

From a quantitative point of view (cf. the figures in Table VI), there is no simple relationship between the ionization potentials (IPs) and the Cr–Cr distances, as had been naively expected. By this statement we mean that the larger change in the Cr–Cr distance (0.080 vs 0.035 Å) occurs where there is the smaller change (0.08 vs 0.52 eV) in the IPs. Moreover, the Cr to ring center distances do not correlate in any direct way with either the Cr–Cr distances or the IPs. This situation becomes less baffling when we note that the *c* axes of the crystals are all different. Of course, this only raises the question of why they are different, but at least it explains why simple relationships, based implicitly on the assumption that the arene to arene distance ($c/2$) is constant and only the donor power of the arene π electrons is being varied, do not show up.

Perhaps the best rationalization of the observations is this. The tendency of the change from benzene to xylene to increase the Cr–Cr distance because xylene is a better donor is partially offset by the fact that the ring centers are now further away (by 0.027 (2) Å) from the Cr–Cr unit. On the other hand, the tendency of the p-$C_6H_4F_2$ to decrease the Cr–Cr distance compared to that in the benzene compound is enhanced by the fact that it is also further away (by 0.048 (2) Å) from the center of the Cr_2 unit. In summary, what seemed in the planning stage like a straightforward experiment (one observable, the Cr–Cr distance, depending on one independent variable, the π-donor capacity of the arene ligand) has been marred by the intrusion of another variable, whose influence cannot be quantified.

It is not clear why the *c* axes change, although there are several possible reasons. It must first be noted that all three compounds crystallize in different space groups. They are closely related and the packing is similar, but small differences (ca. 1%) cannot be considered surprising. Moreover, the packing requirements of the different arene rings may be inherently different, in addition to the fact that they are differently oriented. Finally, there are the unknown effects of the molecules of arene or other solvent that lie between the stacks on which we have focused attention. They differ in number and kind from one case to another,[13] and obviously this could have a small (≤1%) effect on the unit cell dimensions.

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(10) Davy, R.; Hall, M. B. *J. Am. Chem. Soc.* **1989**, *111*, 1268.
(11) Ketkar, S. N.; Fink, M. *J. Am. Chem. Soc.* **1985**, *107*, 338.
(12) Ziegler, T. *J. Am. Chem. Soc.* **1985**, *107*, 4453.
(13) No such molecules were found in the case of the benzene compound,[5] but there could have been some highly disordered, perhaps fractional molecules of benzene present.

Acknowledgment. We thank the National Science Foundation for support.

Supplementary Material Available: Tables of hydrogen atom positions and thermal displacement parameters for $Cr_2(O_2CCPh_3)_4\cdot{}^3/_2C_6H_4F_2$ and for $Cr_2(O_2CCPh_3)_4\cdot C_6H_4Me_2\cdot C_6H_{14}$ and bond distances and angles for the (disordered) lattice hexane molecule in $Cr_2(O_2CCPh_3)_4\cdot C_6H_4Me_2\cdot C_6H_{14}$ (7 pages); tables of observed and calculated structure factors for both compounds (10 pages). Ordering information is given on any current masthead page.

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Preparation of Bis(tetrabutylammonium) Octa(μ_3-chloro)hexakis(trifluoromethanesulfonato)-*octahedro*-hexamolybdate(2−), $(Bu_4N)_2[Mo_6Cl^i_8(CF_3SO_3)^a_6]$: A Versatile Starting Material for Substituted Mo(II) Clusters Containing the $[Mo_6Cl^i_8]^{4+}$ Core

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Received November 8, 1991

The useful starting material $(Bu_4N)_2[Mo_6Cl^i_8(CF_3SO_3)^a_6]$, was synthesized in high yield by the reaction of $(Bu_4N)_2[Mo_6Cl^i_8Cl^a_6]$ with $AgCF_3SO_3$ in CH_2Cl_2. The crystal structure of the benzyltrimethylammonium salt of this cluster reveals an average Mo–Mo distance of 2.593 (4) Å, an average Mo–Cl distance of 2.465 (4) Å, and an average Mo–O distance of 2.126 (9) Å. The triflate ligands, $CF_3SO_3^-$, are readily substituted by other ligands. Convenient routes are reported for the preparation of the clusters $[Mo_6Cl^i_8X^a_6]^{2-}$, X = Cl^-, Br^-, I^-, SCN^-, OMe^-, $CH_3CO_2^-$, $CH_3C_6H_4SO_3^-$, and $CF_3CO_2^-$; the latter three are new. These anionic clusters were characterized by IR, UV–vis and fast atom bombardment mass spectrometry. Solution IR data of the title compound in dimethylformamide are consistent with the complete displacement of the triflate ligands by the solvent, only partial displacement is observed in acetone, and the cluster retains all $CF_3SO_3^-$ ligands in CH_2Cl_2. The isolation of the new cationic clusters, $[Mo_6Cl^i_8L^a_6]$,$^{4+}$ with L = C_5H_5NO, $(C_6H_5CH_2)_2SO$, and $(C_6H_5)_3PO$, as triflate salts is also described. Crystal data for $(BzMe_3N)_2[Mo_6Cl^i_8(CF_3SO_3)^a_6]$ are as follows: triclinic space group, $P\bar{1}$ (No. 2); $a = 11.036$ (2) Å, $b = 11.553$ (3) Å, $c = 12.010$ (2) Å; $\alpha = 79.05$ (2)°, $\beta = 78.06$ (1)°, $\gamma = 86.58$ (2)°; $V = 1471$ (1) Å^3; $Z = 1$.

Introduction

The early d-block halide clusters of group 6, such as $[Mo_6Cl_{14}]^{2-}$ and $[W_6Cl_{14}]^{2-}$, were the first metal clusters to be structurally characterized.[1] Their ligand substitution chemistry has been extensively explored,[2] and metal–metal bonding in these systems has been investigated theoretically.[3] Recently these compounds have been shown to exhibit interesting redox chemistry and photophysical properties.[4] The existence of related groups 4 and 5 clusters[5] and the superconducting Chevrel phases, e.g. $PbMo_6S_8$,[6] adds further interest to the octahedral clusters containing π-donor ligands.

The Mo(II) chloride cluster consists of a substitution resistant core of $[Mo_6Cl_8]^{4+}$ with eight face-bridging inner ligands (labeled i)[7] and six semilabile terminal outer ligands (labeled a).[7] For example, anionic clusters such as $[Mo_6Cl^i_8X^a_6]^{2-}$ (where X = Cl^-, Br^-, I^-, or OH^-) are known as well as neutral compounds of the type $[Mo_6Cl^i_8Cl^a_4L^a_2]$ (where L = a neutral ligand).[2] Many compounds with four outer chlorides and two other outer ligands have been reported, but the replacement of all six chlorides is difficult unless the substituting ligand is another halide or pseudo-halide.[2e,j] Moreover, the synthetic procedures for these compounds are specific for a given class of compounds and occasionally require long reaction times. More labile terminal ligands than chloride are needed to extend and facilitate the preparative chemistry of these interesting clusters. Although the perchlorate ligand has been explored in this context, the explosive nature of this cluster complex greatly decreases the synthetic utility of $[Mo_6Cl^i_8(dmf)^a_6][ClO_4]_4$.[8]

We report the preparation of a new Mo(II) cluster compound having easily replaceable ligands and the crystal structure of the bis(benzyltrimethylammonium) salt and demonstrate the use of $(Bu_4N)_2[Mo_6Cl^i_8(CF_3SO_3)^a_6]$ in the preparation under mild conditions of other clusters containing anionic and neutral ligands. The salt compound $(Bu_4N)_2[Mo_6Cl^i_8(CF_3SO_3)^a_6]$ is soluble in the poorly coordinating solvent CH_2Cl_2, which minimizes competition with ligands.

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(1) (a) Brosset, C. *Ark. Kemi, Mineral. Geol.* **1945**, *20A* (7), 1. (b) Brosset, C. *Ark. Kemi, Mineral. Geol.* **1946**, *22A* (11), 1.

(2) (a) Sheldon, J. C. *Nature* **1959**, *184*, 1210. (b) Sheldon, J. C. *J. Chem. Soc.* **1960**, 1007. (c) Sheldon, J. C. *J. Chem. Soc.* **1960**, 3106. (d) Sheldon, J. C. *J. Chem. Soc.* **1961**, 750. (e) Sheldon, J. C. *J. Chem. Soc.* **1962**, *410*. (f) Carmichael, W. M.; Edwards, D. A. *J. Inorg. Nucl. Chem.* **1967**, *29*, 1535. (g) Fergusson, J. E.; Robinson, B. H.; Wilkins, C. J. *J. Chem. Soc. A* **1967**, 486. (h) Nannelli, P.; Block, B. P. *Inorg. Chem.* **1968**, *7*, 2423. (i) Hamer, A. D.; Smith, T. J.; Walton, R. A. *Inorg. Chem.* **1976**, *15*, 1014. (j) Weissenhorn, R. G. *Z. Anorg. Allg. Chem.* **1976**, *426*, 159. (k) Michel, J. B. *ERDA Energy Res. Abstr.* **1977**, *2*, No. 39967. (l) Kraft, J.; Schäfer, H. *Z. Anorg. Allg. Chem.* **1985**, *524*, 137. (m) Schäfer, H.; Plautz, H.; Abel, H.-J.; Lademann, D. *Z. Anorg. Allg. Chem.* **1985**, *526*, 168. (n) Saito, T.; Nishida, M.; Yamagata, T.; Yamagata, Y.; Yamaguchi, Y. *Inorg. Chem.* **1986**, *25*, 1111. (o) Chisholm, M. H.; Heppert, J. A.; Huffman, J. C. *Polyhedron* **1984**, *3*, 475.

(3) (a) Crossman, L. D.; Olsen, D. P.; Duffey, G. H. *J. Chem. Phys.* **1963**, *38*, 73. (b) Cotton, F. A.; Haas, T. E. *Inorg. Chem.* **1964**, *3*, 10. (c) Kettle, S. F. A. *Theor. Chim. Acta* **1965**, *3*, 211. (d) Guggenberger, L. J.; Sleight, A. W. *Inorg. Chem.* **1969**, *8*, 2041. (e) Cotton, F. A.; Stanley, G. G. *Chem. Phys. Lett.* **1978**, *58*, 450. (f) Bursten, B. E.; Cotton, F. A.; Stanley, G. G. *Isr. J. Chem.* **1980**, *19*, 132. (g) Azumi, T.; Saito, Y. *J. Phys. Chem.* **1988**, *92*, 1715.

(4) (a) Maverick, A. W.; Gray, H. B. *J. Am. Chem. Soc.* **1981**, *103*, 1298. (b) Maverick, A. W.; Najdzionek, J. S.; MacKenzie, D.; Nocera, D. G.; Gray, H. B. *J. Am. Chem. Soc.* **1983**, *105*, 1878. (c) Nocera, D. G.; Gray, H. B. *J. Am. Chem. Soc.* **1984**, *106*, 824. (d) Mussell, R. D.; Nocera, D. G. *Polyhedron* **1986**, *5*, 47. (e) Jackson, J. A.; Turro, C.; Newsham, M. D.; Nocera, D. G. *J. Phys. Chem.* **1990**, *94*, 4500.

(5) Rogel, F.; Corbett, J. D. *J. Am. Chem. Soc.* **1990**, *112*, 8198, and references therein.

(6) (a) Chevrel, R.; Sergent, M.; Prigent, J. *J. Solid State Chem.* **1971**, *3*, 515. (b) Chevrel, R. In *Superconductor Materials Science: Metallurgy, Fabrication and Applications*; Foner, S., Schwartz, B. B., Eds., Plenum: New York, 1981; Chapter 10. (c) Chevrel, R.; Hirrien, M.; Sergent, M. *Polyhedron* **1986**, *5*, 87.

(7) Schäfer, H.; Schnering, H. G. *Angew. Chem.* **1964**, *76*, 833.

(8) Cotton, F. A.; Curtis, N. F. *Inorg. Chem.* **1965**, *4*, 241.

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